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MANUFACTURE OF DENSE SINTERED BODIES CONTAINING SILICON NITRIDE

K. Hirota, Y. Hasegawa, K. Ogura, Y. Yashima

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16. Abstract  Sintered bodies containing 1-32.5 Si oxide and >1.5 wt.% SiC (Si oxide/SiC wt. ratio <3/2) are prepared and kept in a 10-3000 kg/cm <sup>2</sup> N (g) atmosphere at 1500-2300 degrees, while simultaneously maintaining the CO (g) partial pressure around the body lower than the nitrogenation equil. pressure to give a dense sintered body. The prepared dense sintered body has high strength at high temperatures. Thus, SiC 40, Si oxide 30 and Si <sub>3</sub> N <sub>4</sub> 30 wt% were fired to a body which was kept in 1500 kg/cm <sup>2</sup> N (g) for 20 h at 2000 degrees to give a dense sintered body having high bending strength at high temperatures.			
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(54) Method for Manufacture of Dense Sintered Bodies Containing  
Silicon Nitride

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(72) Inventor: K. Hirota  
11-4, 2-chome, Takesono  
Sakuramura, Shinji-kun  
Ibaraki-ken

(72) Inventor: Y. Hasegawa  
3-8, Hoku, 3-chome, Nakamura,  
Nerima-ku, Tokyo

(72) Inventor: K. Ogura  
110-103, 3-chome, Takesono, Sakuramura  
Shinju-kun, Ibaraki-ken

(72) Inventor: Y. Yashima  
104-202, 3-chome, Takesono,  
Sakuramura, Shinji-kun, Ibaraki-ken

(71) Applicant: Head, Inorganic Materials Research Institute  
Office of Science and Technology  
Kagaku Kijutsu-cho

# MANUFACTURE OF DENSE SINTERED BODIES CONTAINING SILICON NITRIDE

K. Hirota, Y. Hasegawa, K. Ogura, Y. Yashima

Detailed Specifications

/427\*

## 1. Name of Invention:

Method for Manufacture of Dense Sintered Bodies Containing Silicon Nitride

## 2. Scope of Patent Claims

Manufacture with a method characterized by use of sintered bodies from a compound which contains 1-32.5 wt% silicon carbide, and which also has a ratio of three parts silicon oxide to two or more parts silicon carbide; and by keeping the body in nitrogen gas at 10-3000 kg/cm<sup>2</sup> and 1500-2300°C while simultaneously maintaining the carbon monoxide partial pressure around the body lower than the nitrogenation equilibrium pressure.

## 3. Detailed Explanation of the Invention

This invention concerns a method of manufacturing dense sintered bodies which contain silicon nitride and which, more specifically, exhibit a high degree of strength at temperatures above 1200°C.

Sintered bodies of silicon nitride, or with silicon nitride as one ingredient and silicon carbide, etc., as the others, are superior in hardness and chemical stability, do not lose their

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\*Numbers in the margin indicate pagination in the foreign text.

rigidity at high temperatures, show a high degree of strength, and almost never break because of thermal shock. This has lead to the expectation that they might be used as heat- resistant materials.

They have not, however, exhibited properties commensurate with the abovementioned expectations. This is due to the fact that, when the powdered material is being sintered into a molded form, the agent added to aid the sintering process acts to decrease the strength of the sintered body at high temperatures. This occurs when the silicon oxide contained as an auxiliary agent in the material undergoing sintering combines with such substances as  $MgO$ ,  $Y_2O_3$ , or  $CaO$ , thereby forming solid-phase oxides with a low melting point and, consequently, lowering the high-temperature strength of the sintered body. In addition, even though there exists a method for making a comparatively pure silicon nitride sintered body by means of nitrogenating elemental silicon powder, the body obtained with this method does not attain a full degree of strength because of vacancies left within it.

This invention eliminates these problems by providing a manufacturing method which does not allow material which vitiates high-temperature strength to remain in the body and which, by attaining a full degree of density, produces a body with a high degree of high-temperature strength.

The inventors took experimental results which would lead to attaining the aforementioned goals and put the invention into final form by using a certain quantity of silicon oxide as an auxiliary agent for sintering, then making a sintered /428 body containing a certain percentage of silicon carbide, giving the body high-heat treatment in nitrogen gas at high pressure, and expelling the carbon monoxide produced. Once this was accomplished, the resulting sintered body was highly dense and contained no

silicon oxide and, therefore, had superior high-temperature strength.

The distinguishing features of the invention are:

Making a high-density sintered body with a silicon oxide content of 1-32.5 wt% and a silicon carbide content of 1.5 wt% or above, with a ratio of three parts (by weight) silicon oxide to two or more parts silicon carbide, and keeping the sintered body in nitrogen gas at 10-3000 kg/cm<sup>2</sup> and 1500-2300°C while simultaneously keeping the carbon monoxide partial pressure around the body below the nitrogenation equilibrium pressure.

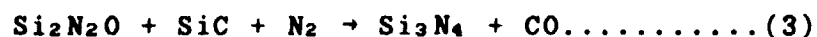
Acid salts of silicon may be used instead of the silicon oxide powder as an ingredient in this invention.

It is desirable for the silicon oxide powder to be spread evenly over the surface of the silicon carbide particles. For example, it is desirable for the surfaces of the silicon carbide powder particles to be covered with a film of silicon oxide while oxidation takes place. This minimizes the occurrence of the miniscule sintering faults which are caused by structural irregularities. It is desirable for the silicon oxide content to be within 1-32.5 wt% and the silicon carbide content to be above 1.5 wt%. Less than 1% silicon oxide would create problems with density, while more than 32.5% is not necessary to attain the desired density, and could have negative effects during the latter stages of the prolonged nitrogenation treatment. Since less than 1.5% silicon carbide would cause the presence of unreacted SiO<sub>2</sub>, a ratio of 3 parts silicon oxide to at least two parts silicon carbide must be maintained. This is so that when the reaction between SiO<sub>2</sub>, SiC and N<sub>2</sub> is complete, some SiC, but no SiO<sub>2</sub>, will remain in the sintered body.

The powdered ingredients which are subjected to sintering may, in addition to silicon oxide and silicon carbide, have silicon nitride and such metallic oxides as alumina, zirconia, etc., mixed into them as needed.

No special conditions are required for sintering, but a moist hydrogen atmosphere, which facilitates the process, is desirable. Under such conditions there are up to 1000 ppm of water present in the silicon oxide, which reduces the viscosity of the silicon oxide and facilitates sintering. Densification should reach the extent at which vacancies take the form of independent bubbles forming within the sintered body. When such bubbles form, they shrink and disappear during the high-temperature, high-pressure nitrogenation treatment.

When the sintered body thus obtained is kept in nitrogen gas at 10-3000 kg/cm<sup>2</sup> and 1500-2300°C, the temperature and pressure cause the silicon oxide and silicon carbide contained in the body to react with the nitrogen. This chemical reaction takes place as shown below.



In these formulas the silicon oxide is represented by SiO<sub>2</sub>. Though variation in composition of ingredients for sintering may occasion the use of a silicon acid salt or metallic acid salts instead of silicon dioxide, use of these other substances is also represented by SiO<sub>2</sub>. The phases of silicon dioxide nitrogenation include not only silicon nitride (Si<sub>3</sub>N<sub>4</sub>), but, since complex compounds frequently form, also include both Si<sub>3</sub>N<sub>4</sub> and Si<sub>2</sub>N<sub>2</sub>O. Furthermore, in this



invention, when silicon nitride is mentioned, both  $\text{Si}_3\text{N}_4$  and  $\text{Si}_2\text{N}_2\text{O}$  are included.

As shown in the formulas, the oxygen in the silicon oxide contained in the sintered body combines with the carbon in the silicon carbide particles to produce carbon monoxide gas. The nitrogen, on the other hand, combines with the available silicon to form silicon nitride.

The use of HIP treatment, that is, the use of gas at high temperature and high pressure to force gas bubbles out of sintered bodies, has already been discovered. The material usually used for this method is argon gas, though nitrogen gas has also been used.

The nitrogenizing method used in this invention is /429 different from the HIP treatment in the following ways:

(1) First, in this invention more than 1 wt% of silicon oxide is included in the body which undergoes sintering. Since the silicon oxide has a low degree of high-temperature strength, and sintered bodies which contain a large amount of it are not suitable for use as heat-resistant materials, inclusion of this substance is restricted. In this invention, it is necessary to include more than 1 wt% because the silicon oxide is used together with silicon carbide and transformed into silicon nitride, which has a high degree of high-temperature strength.

(2) The second point concerns expulsion of the carbon monoxide produced during nitrogenation and the maintenance of the carbon monoxide partial pressure around the sintered body at a level below that of the equilibrium pressure for the reaction. If this were not done, the reactions described in the formulas above would not continue until nitrogenation was complete. The

carbon monoxide equilibrium pressure is expressed as a function of the nitrogenation temperature in Figure 1. When using a nitrogen pressure of 1000 kg/cm<sup>2</sup>, the carbon monoxide partial pressure at 1500°C is 200 kg/cm<sup>2</sup>, and at 2000°C it would be 410 kg/cm<sup>2</sup>, showing the tendency for carbon monoxide partial pressure to increase as temperature increases. Keeping carbon monoxide partial pressure low causes the gases around the body undergoing sintering to flow, and makes the nitrogen flow in where carbon monoxide partial pressure is low. The process whereby silicon oxide and silicon carbide interact, allowing nitrogenation to take place, proceeds in two stages, as shown in formulas (2) and (3). That is to say, in addition to the reaction shown in Formula (1), a sequence is followed whereby the reaction in Formula (2) produces a compound containing both oxygen and nitrogen, and then the reaction in formula (3) produces a nitride. In the latter case, if reaction (2) proceeds rapidly and reaction (3) is delayed because carbon monoxide partial pressure has not been fully lowered, it is easy for a situation to arise in which the carbon monoxide is not promptly expelled. It is, however, permissible to stop with reaction (2) and have a sintered body composed mainly of Si<sub>2</sub>N<sub>2</sub>O. For reaction (3) - complete nitrogenation - to take place, if nitrogen partial pressure is 1000 kg/cm<sup>2</sup>, carbon monoxide partial pressure should be kept at 0.5 kg/cm<sup>2</sup>, or, even better, below 0.1 kg/cm<sup>2</sup> in order for the reaction to proceed very rapidly. The nitrogenation temperature must be within the 1500-2300°C range. Since silicon oxide softens at about 1500°C and melts above 1740°C, nitrogenation would be difficult at temperatures below 1500°C, and the best range is above 1700°C. Since silicon nitride decomposes at temperatures above 2300°C, it is necessary to stay below this point.

Required time for nitrogenation at 1750°C is more than 10 hr. Higher temperatures decrease the time required. If, however, the temperature is too high, the body undergoing treatment may form coarse crystals.

In order to prevent coarse crystallization, the silicon carbide content should exceed 2/3 that of silicon oxide, and it is preferable to leave some excess of silicon carbide in the sintered body. Generally, a processing time not exceeding thirty minutes and a low processing temperature yield a good-quality sintered body.

#### Experiment

A sintered body with a vacancy ratio of less than 1% was made by taking a powdered mixture with particle diameter of 1  $\mu$ , composed of 40 wt% silicon carbide, 30 wt% silicon oxide and 30 wt% silicon nitride. This mixture was treated for 10 min. at 1700°C under 30 kg/cm<sup>2</sup> pressure. A sample in the form of a square column measuring 4\* by 40\* was cut out and kept in circulating nitrogen at 1500 kg/cm<sup>2</sup> and 2000°C for 20 hr. A 28-H -type sintered body composed entirely of silicon nitride was obtained. The three-point bending strength of this sample at 1300°C was 52 kg/mm<sup>2</sup>.

As shown above, this invention makes it possible to manufacture a sintered body with a high degree of high-temperature strength and high density.

#### 4. Explanation of Illustration

The illustration shows carbon monoxide partial pressure (the result of the reaction in which silicon carbide, silicon oxide and nitrogen produce silicon nitride and carbon monoxide) as a function of temperature.

[\*Translator's note: Illegible word, perahps mm.]

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